COMMONWEALTH OF KENTUCKY BEFORE THE PUBLIC SERVICE COMMISSION

In the Matter of:

B.T.U. PIPELINE, INC.))) CASE NO. 96-087
ALLEGED FAILURE TO COMPLY WITH COMMISSION REGULATIONS))

ORDER

On January 25, 1996, a portion of the natural gas facilities of B.T.U. Pipeline, Inc. ("B.T.U.") were inspected by the Commission's Gas Pipeline Safety Investigators. The inspection took place on a segment of B.T.U.'s facilities directly connected to the "Stevens" well on Kentucky Route 7 between Salyersville and Royalton, Kentucky near the Stevens Cemetery. During the inspection, a sample of the pipeline gas was taken from a drip tank serving two residential meters and tested for the presence of hydrogen sulfide ("H₂S"). H₂S was present at 1,000 parts per million. Commission regulation 807 KAR 5:022, Section 15, permits no more than a trace of H₂S. The results of this inspection were reduced to a report which is attached as Appendix A.

The owner and operator of B.T.U., Richard Williams, was contacted the same day and instructed to shut in the well to terminate the flow of gas into B.T.U.'s facilities. Mr. Williams indicated that he would close the valve to the well. Commission safety inspectors returned on January 31, 1996 to test again for the presence of H₂S and found the levels of H₂S had dropped to 200

ppm. Further samples were taken on February 8, 1996 and confirmed the levels of $\rm H_2S$ had continued to drop to 60 ppm. The results of these two inspections were reduced to a report which is attached as Appendix B.

The presence of H_2S in natural gas is a serious threat to public health and safety. At levels half those found on the B.T.U. system, serious damage to the nervous system and cessation of breathing within 15 minutes can occur from limited exposure. At 1,000 parts per million, the level detected on the B.T.U. system, unconsciousness and immediate death can occur. Also, H_2S is corrosive to iron-based materials and causes metal to crack.

Although Richard Williams agreed to terminate the gas supply contaminated by H_2S by closing the valve at the well, it will remain possible to reintroduce the sour gas by merely opening the valve. The connection to the well should be completely severed to remove the threat to the public safety.

Based upon the foregoing, the Commission finds that a prima facie showing has been made that B.T.U. and Richard Williams, in his individual capacity as owner and operator, have violated 807 KAR 5:022, Section 15, in allowing gas contaminated with high levels of $\rm H_2S$ to enter its gas supply and subjecting its residential customers and its employees to potentially life threatening levels of $\rm H_2S$.

IT IS THEREFORE ORDERED that:

1. Richard Williams, individually, and B.T.U. shall appear, represented by counsel, before the Commission on May 23, 1996, at

10:00 a.m., Eastern Daylight Time, in Hearing Room 1 of the Commission's offices at 730 Schenkel Lane, Frankfort, Kentucky, to show cause why civil fines of up to \$500,000 should not be assessed pursuant to KRS 278.992(1) against Richard Williams or B.T.U., or both, for the pipeline safety violations noted herein.

2. Within 7 days of the date of this Order, Richard Williams or B.T.U., or both, shall completely sever all connections between the contaminated well and the B.T.U. gas system in the presence of a Commission gas safety inspector.

Done at Frankfort, Kentucky, this 14th day of March, 1996.

PUBLIC SERVICE COMMISSION

Chairman

Wigo Chairman

ATTEST:

Executive Director

COMMONWEALTH OF KENTUCKY PUBLIC SERVICE COMMISSION

INSPECTION REPORT

B.T.U. PIPELINE, INC.

JANUARY 26, 1996

BRIEF

An inspection of a portion of the natural gas facilities of B.T.U. Pipeline, Inc. ("B.T.U.") was conducted on January 25, 1996. B.T.U. is a natural gas distribution company in Magoffin County, Salyersville, Kentucky. This inspection was conducted in accordance with the Public Service Commission's ("PSC") policy of inspecting all natural gas operators under its jurisdiction. Natural gas operators are jurisdictional to the PSC under KRS 278.040 and also through a 5(a) Agreement with the United States Department of Transportation, Office of Pipeline Safety, for compliance to the Natural Gas Pipeline Safety Act of 1968.

INSPECTION

During the inspection, a sample of the pipeline gas was drawn through a Draker tube to test for the presence of hydrogen sulfide (" H_2S ") in the gas stream. The sample was taken at the residence of Charles Stevens on Highway 7 in Royalton, Kentucky. The staining of the Draker tube indicated that H_2S was present at 1000 parts per million ("ppm").

The following comments are excerpts from the U.S. Safety Services, Inc., The Hydrogen Sulfide Safety Manual, (Attachment 1), and an article from the January 4, 1988 Oil and Gas Journal (Attachment 2) regarding $\rm H_2S$:

100 ppm - At this level, sense of smell is lost in 3-5 minutes and eyes and throat may burn.

Report - B.T.U. Pipeline, Inc. Page 2 January 26, 1996

500 ppm - At this concentration, the effects on the nervous system result in loss reasoning and balance and will lead to cessation of breathing within 15 minutes.

1000 ppm - Exposure at this level results in immediate unconsciousness and leads quickly to death.

 ${\rm H}_2{\rm S}$ in the presence of small amount of oxygen and water forms sulfuric acid which promotes aggressive corrosion of iron-based materials.

The following is taken from an article by Neal Adams, Don Carter, and Larry Ingram (Attachment 3) concerning H_2S in the drilling industry.

Characteristics of Hydrogen Sulfide Gas

- 1. H₂S is colorless.
- 2. Odor of rotten eggs; however, at 50 ppm, the sense of smell is deadened.
- 3. Specific gravity of ${\rm H}_2{\rm S}$ is 1.192 causing the gas to settle in low areas.
- 4. Explosive range is 4.3 to 45 percent as compared to methane gas at 5 to 15 percent.
- 5. $\rm H_2S$ has an ignition point of 500° Fahrenheit compared to Methane at 1000° Fahrenheit.
- 6. ${\rm H}_2{\rm S}$ when burned produces sulfur dioxide, another toxic gas.

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January 26, 1996

Table 2 - Effects of H₂S on Personnel

- 1. 10 ppm Can smell at this level, safe for 8 hours.
- 2. 100 ppm Kills smell in 3 to 15 minutes, may burn eyes and throat.
- 3. 200 ppm Kills sense of smell quickly, burns eyes and throat.
- 4. 500 ppm Loss of balance, respiratory difficulties in 30 to 45 minutes.
- 5. 700 ppm Unconscious in less than 15 minutes; death will occur if not rescued promptly.
- 6. 1000 ppm Permanent brain damage, if not rescued immediately.

FINDINGS

The following deficiency was found: 807 KAR 5:022, Section 15, allows no more than a trace of $\rm H_2S$.

RECOMMENDATIONS

It is recommended that given the danger, both, to the public and B.T.U. employees, B.T.U. must immediately terminate the flow of gas until the source of the H_2S is found and removed from the gas stream.

Respectfully submitted,

David B. Kinman

Gas Utility Investigator

DBK:dcp/9602100

APPENDIX A

AN APPENDIX TO AN ORDER OF THE KENTUCKY PUBLIC SERVICE COMMISSION IN CASE NO. 96-087 DATED MARCH 14, 1996



COMMONWEALTH OF KENTUCKY PUBLIC SERVICE COMMISSION

730 SCHENKEL LANE POST OFFICE BOX 615 FRANKFORT, KY. 40602 (502) 564-3940

January 26, 1996

Mr. Richard Williams, Owner B.T.U. Pipeline, Inc. P. O. Box 242 Salyersville, Kentucky 41465

Dear Mr. Williams:

1 some

Attached is an inspection report of a specialized inspection of a portion of the natural gas facilities of B.T.U. Pipeline, Inc., which was performed by David B. Kinman on January 25, 1996.

Please respond to this report by February 27, 1996, outlining a correction schedule of the cited deficiency for Commission approval.

If you have any questions or need additional information, please contact David B. Kinman at (502) 564-3940.

Sincerely,

É. Scott Smith, Manager Gas Pipeline Safety Branch

ESS:DBK:dcp 9602100

Attachment



The Hydrogen Sulfide Safety Manual

He Cappy CPBVIFEC INF

Brookhaven, Mississippi 601-833-7509

Introduction

Hydrogen sulfide gas (H₂S) is a toxic, poisonous gas and is a growing concern in the petroleum industry. Other professions such as miners, sewer maintenance crews, manufacturers of artificial silks and chemicals, and blasters using black powder also fear this gas.

In the petroleum industry new fields are being developed in addition to old fields known to contain H2S. Therefore, workers in these areas can expect an increase in their chances of being exposed to the gas. Federal and state laws are being implemented to insure worker's as well as the public's safety when hydrogen sulfide is a potential threat.

With today's modern technology, equipment, training, and established guidelines, death and injury from H2S exposure are unnecessary. Although H2S is a very toxic, poisonous gas, it can be worked in safely. Therefore, by utilizing our knowledge and exercising the proper precautionary measures, we shouldn't have a single injury from hydrogen sulfide exposure.

But REMEMBER — your safety program will only be as effective as you conscientiously make it. It only takes one careless person to render a "safe" program "UNsafe".

Physical Characteristics and Description of H₂S

1. Scientific Name -Hydrogen Sulfide Chemical Formula ,—H₂S

-Sour Gas, Rotten Egg Gas, Common Names Sulphur Gas, Poison Gas, Sulfuretted Hydrogen

2. Color	—No color. Just like the air that surrounds you, it cannot be
•	seen.
3. Odor	-Very offensive. Commonly
	referred to as the "odor of rot
	ten eggs".
4. Weight	—H₂S has a vapor density of
	1.189 and is heavier than air
	(1.0). The gas will settle and
	accumulate in low lying areas
Explosive Limits	—H₂S will form an explosive

6. Ignition Byproducts

7. Solubility

8. Corrosiveness

- —H₂S will form an explosive mixture with air in concentrations between 4.3 and 46 percent by volume. It has an automatic ignition point of 500° F. and once ignited, burns with a blue flame. Vapors may travel a considerable distance to a source of ignition and flashback.
- —Once ignition occurs the H₂S is converted to Sulphur Dioxide (SO₂) and water vapor. Do not assume an area is safe after ignition because sulphur dioxide is also a very toxic gas.
- H₂S is soluble in both water and liquid hydrocarbons.
 H₂S is corrosive to all electrochemical series metals. It can also cause hydrogen embrittlement in steel pipe having a tensile strength of

95,0000 psi or more.

Relative Toxicity

 $\rm H_2S$ is an extremely toxic gas. It is ranked second to hydrogen cyanide, a gas used in the "gas chamber" for the execution of convicted criminals. $\rm H_2S$ is five to six times more toxic than carbon monoxide, an exhaust gas commonly associated with autos.

The following table gives a comparison of the toxicity of H₂S and SO₂ to other very poisonous gases.

Common Name	Chemical Formula	Specific Gravity SG Air = 1	Threshold ¹ Limit	Hazardous ² Limit	Lethal ³ Concen- tration
Hydrogen Cyanide	HCN	0.94	10 ppm	150 ppm/hr	300 ppm
Hydrogen Sulfide	н,ѕ	1.18	10 ppm ⁴ 20 ppm	250 ppm/hr	600 ppm
Sulfur Dioxide	SO ₂	2.21	5 ppm	_	1000 ppm
Chlorine	CI,	2.45	1 ppm	4 ppm/hr	1000 ppm
Carbon Monoxide	СО	0.97	50 ppm	400 ppm/hr	1000 ppm
Carbon Dioxide	CO2	1.52	5000 ppm	5%	10%
Methane	CH₄	0.55	90,000 ppr	n Combustible above 5% in air	•

¹Threshold limit - concentration at which it is believed that all workers may be repeatedly exposed day after day without adverse effects.

²Hazardous limit - concentration that may cause death.

³Lethal concentration - concentration that will cause death with short-term exposure.

⁴Threshold limit = 10 ppm - 1972 ACGIH (American Conference of Governmental Industrial Hygienists)

^sThreshold limit = 20 ppm — 1966 ANSI acceptable ceiling concentration for eight-hour exposure (based on 40-hour week) is 20 ppm. OSHA Rules and Regulations (Federal Register, Volume 37, No. 202, Part II, dated October 18, 1972.)

Physical Effects On Humans

The principal hazard is by inhalation. When the amount of gas absorbed into the bloodstream exceeds the bloodstream's oxidation capacity, systemic poisoning results. The resulting symptoms will depend on the physiological make-up of the individual, the concentration of H_2S breathed, and the volume of the concentration breathed.

Depending on these factors, the following symptoms may be seen individually or in combinations: headache, dizziness, excitement, nausea, coughing, drowsiness, burning sensation in the eyes, nose, and throat, and labored respiration with respiratory paralysis at higher concentrations.

NOTE: THE SENSE OF SMELL IS QUICKLY PARALYZED BY H₂S. DO NOT RELY ON THE SENSE OF SMELL AS A METHOD OF DETECTION.

The following chart has been prepared to give an idea of what effects H₂S may have on an individual at varying concentrations. Keep in mind that these are relative reactions. Every individual, due to his different body make-up, will respond a particular way to a particular concentration of H₂S. Repeated exposure to H₂S has no documented cumulative effect and therefore neither increases or decreases an individual's future susceptibility to H₂S.

Since this chart deals in parts-per-million (ppm), to give an example of how small one (1) ppm actually is:

If time were equated in terms of ppm, then 1 ppm would be the equivalent of taking 1 second out of 11 1/2 days.

Hopefully, this will help put into perspective the term "ppm".

Physical Effects

and

is flammable. It is heavier than air

a colorless and transparent gas and itow places.

Grains, Grains, Percent (%) PPM 100 std. ft. 31 0.00002
100 6.48 200 12.96 500 32.96 700 45.36
NCITIES

REMEMBER: 1% = 10,000 Parts Per Million (PPM).

At 15.00 psia and 60°F.

Hydrogen Sulfide is may accumulate in It

5

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Detection

There are several detection devices available for alerting personnel to the presence of H₂S. When testing, always be prepared to encounter lethal concentrations of the gas.

NOSE — DO NOT RELY ON YOUR NOSE AS A METHOD OF DETECTION.

You can smell as little as 1 ppm of H_2S but as the concentration approaches the 150 ppm range, your sense of smell is quickly deadened giving a false sense of security. Anytime anyone smells "rotten eggs", they should immediately hold their breath, proceed upwind and/or don their protective breathing equipment, and notify their supervisor. **DO NOT HESITATE.**

AMPOULES, SPOT CHECKS — These detection devices change color usually from white to a brown or black due to lead sulfide being formed from the reaction of lead acetate with hydrogen sulfide. These are not accurate, only applicable in low concentrations of H₂S, and should only be used as an indicator.

HAND OPERATED MECHANICAL AIR SAMPLING TUBE DETECTORS — This device consists of a pump which draws a known volume of the gas being sampled through a graduated tube containing selica gel granules coated with various reagents. Tubes are available for testing both H₂S and SO₂ gases. The presence of the gas being tested will be shown as a gradual color change of the granules. For proper color changes, correction factors, and accuracy information, leaflets accompany each box of tubes and should be read carefully before attempting a test.

There are several reliable hand-held detectors available, but their accuracy will depend on the training and practice of the operator. **DO NOT** test for H₂S or SO₂ unless you are prepared to encounter lethal concentrations.

PERSONAL ELECTRONIC MONITORS — These portable units vary in design and function but will continuously monitor for H₂S at the sensor head. Should H₂S be encountered, at a preset concentration an audible alarm will be activated and certain models will also give a readout.

FIXED MONITORING SYSTEMS — These systems continuously monitor for H₂S at key points and once preset concentrations are detected, visual and audible alarms are triggered to warn personnel. Once a concentration has been detected, the hand-held tube detector may be used to confirm the electronic monitor's reading. Irregardless of the fixed monitoring system reading, wear protective breathing equipment when making tests.

TUTWILER METHOD — This is an extremely accurate method for testing very low to very high concentrations of H₂S. It involves a titration process and requires special apparatus for conducting.

Protection

1

Once concentrations of H₂S have exceeded 20 ppm, the usage of protective breathing equipment becomes essential. It is of utmost importance that potential users of self-contained breathing apparatus know the limitations, intended use, availability, location, maintenance, and applicable rules and regulations pertaining to the equipment.

There are basically three categories of self-contained breathing apparatus available.

ESCAPE UNITS — This unit is also referred to as an air capsule and generally characterized by a clear elasticized enclosure which fits around the neck totally covering the head. These units are designed to supply enough air to allow you to escape to a safe breathing area in the event of an emergency.

WORK UNITS — By design, these units allow the user to work for extended periods of time in toxic atmospheres and the weight of the unit considerably lessens worker fatigue. Breathable air is supplied via an airline from an approved air supply. This unit also has an escape bottle designed to allow the user passage to a safe breathing area should conditions warrant such action.

RESCUE UNITS — This unit limits the user to a thirty-minute supply of air. Also referred to as a "back pack", this unit allows the user unlimited mobility, can also be used as a work unit, and is utilized should someone be overcome by H₂S necessitating an emergency rescue. An audible alarm sounds when approximately 5 minutes of air is left, thus allowing the user enough time to return to a safe breathing area.

Note: Here again, due to the different physiological makeup of individuals, the total amount of "air time" gotten out of a self-contained breathing apparatus will vary from user to user. The primary factors effecting time are physical condition, physical size, amount of physical activity being performed, and the mental state of the user.

Physical Limitations: The following conditions must be adhered to when using self-contained breathing apparatus:

- 1. Facial hair must not interfere with a proper face seal.
- Eye glass templates can not pass between the mask and face.
- 3. Dentures should be worn to insure a proper seal.
- Contact lenses should not be worn in toxic atmospheres with supplied air respirators.

REMEMBER: Anytime concentrations of H₂S have exceeded 20 ppm, you must don your protective breathing equipment which will protect you only when you use it properly. And for it to function properly, it must be regularly cleaned, inspected and repaired when necessary. Never store breathing equipment partially filled, empty, or with the straps tightened. In an emergency, improperly maintained equipment could cost a man his life.

Safety Systems and Devices

BUDDY SYSTEM — Once H₂S begins breaking out into the atmosphere, workers should begin working in pairs. This means under no circumstances should anyone go anywhere without letting someone know where he is going and watching him if necessary. This system is only effective when full participation occurs.

SAFETY BELTS AND RETRIEVAL ROPES — Should work necessitate a worker(s) going into a potentially high risk area, then a lifeline should be secured to a safety belt in the event emergency retrieval is necessary. Also, when going into enclosed spaces or descending into potentially high risk areas, workers should wear lifelines.

WARNING SIGNS — Various warning signs should be located at key entrances and around the rig. It is important for workers to be aware of the location of these signs, their purpose, and of course, to obey the warnings.

BRIEFING AREAS — At least 2 safe briefing areas will be designated on location. Preferably the Number 1 Safe Briefing Area will be established upwind from the well according to the prevailing wind direction. The other safe briefing area should be set perpendicular to the wellbore from the Number 1 Safe Briefing Area.

In the event of an emergency, personnel not pertinent to well control can gather in the upwind safe briefing area to make certain everyone is accounted for and to await further instructions from the supervisor in charge.

Normally, additional breathing and safety equipment is located at the safe briefing areas.

CASCADE SYSTEMS — Cascade systems are the breathable air source which supplies air to the work units discussed earlier. They normally consist of various numbers of 300 cubic feet cylinders manifolded together with a high/low pressure regulator to reduce the air pressure going to the low pressure manifolds in strategic work areas. The number of cascade systems varies with location size and low pressure system lay-out.

WIND INDICATORS — Concentrations of H₂S can be rapidly dispersed by the wind, depending on wind velocity and H₂S concentrations and volumes. To determine wind direction, windsocks and windstreamers should be installed around the location. Also flags, smoke from engines, smoke from flares, and steam rising from the "possum belly" and mud pit area can be good wind direction indicators.

ALL PERSONNEL SHOULD DEVELOP WIND DIRECTION CONSCIOUSNESS.

RIG FANS — On calm days or nights, rig fans can be utilized to help disperse H_2S concentrations effectively in the work area. In addition to reducing the respiratory hazard, the use of rig fans can lessen the chance of combustible concentrations accumulating.

FLARE GUN — In the event of an H₂S release and after all procedures have been attempted to repair the leak source, if it has been determined that:

- 1. Human life is in danger.
- There is no hope of controlling the leak or blowout under the prevailing conditions, then the supervisor in charge may use the flare gun to ignite the well.

The flare gun may also be used for igniting a flare should the flare pilot light fail. Sometimes due to the small volume of gas being flared, it is very hard to successfully light the flare using a flare pistol.

Emergency Rescue and First Aid

With the proper safety system, professional training, and the desire on everyone's behalf to maintain the "safest" safety program, injuries from H₂S exposure should be non-existant. However, should someone be overcome or effected by H₂S, then the preparedness and immediate action of his fellow workers can very well be the key to his survival.

The proper procedure for executing an emergency rescue follows:

- 1. When someone sees a fellow worker overcome or being overcome by H₂S, perhaps his initial instinct may be to run into the toxic area and drag the victim to a safe breathing area. This could cost the would-be rescuer his life, as well as the victim's. Remember: ALWAYS put on PROPER rescue respiratory equipment before attempting a rescue. Try to attract other's attention to the fact that someone has been overcome by H₂S.
- After checking the wind indicators, move the victim to fresh air at once..... UPWIND OR CROSSWIND AWAY from the wellbore or source of gas.
- 3. If: The victim is **not** conscious The victim is **not** breathing

Then: Mouth-to-mouth respiration should be administered immediately. Continue until an oxygen resusitator is brought in or normal breathing is restored.

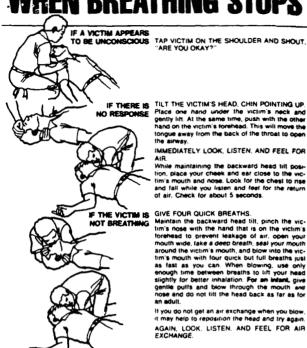
- 4. After reviving a victim: Keep the victim lying down. Cover him only enough to keep him from losing body heat. (It is better for him to be slightly cool than toasty warm.)
- 5. Call for medical help/doctor as soon as possible.
- DO NOT leave the victim unattended until medical help arrives.

REMEMBER: The average person will die in 4 to 6 minutes or less if his oxygen supply is cut off. Many times it is impossible to tell exactly when a person stopped breathing. He may be very near death when you first discover him. Therefore, you should always start artificial respiration **AS SOON AS POSSIBLE.** The objectives of artificial respiration are:

- To maintain an open airway through the mouth and nose.
- 2. To cause air to flow in and out of the lungs.

The following Red Cross suppliment gives an illustrated step-by-step procedure for properly administering mouth-to-mouth resuscitation. Due to the common use of chewing tobacco, snuff, etc. in the oil patch, after tapping the victim on the shoulder and shouting "Are you okay?", if there is no response then quickly before executing the head tilt, visually check the victim's mouth for any foreign matter. Remove any foreign matter by sweeping it out using your finger and then execute the head tilt.

WHEN BREATHING STOPS



TILT THE VICTIM'S HEAD, CHIN POINTING UP. Place one hand under the victim's neck and gently lift. At the same time, push with the other hand on the victim's forehead. This will move the longue away from the back of the throat to open

IMMEDIATELY LOOK, LISTEN, AND FEEL FOR

le maintaining the backward head tilt posi-place your cheek and ear close to the vic-s mouth and nose. Look for the chest to rise fall while you listen and feet for the return ir. Check for about 5 seconds.

GIVE FOUR QUICK BREATHS.
Maintain the backward head tilt.
Itm's nose with the hand that is

AGAIN, LOOK, LISTEN. AND FEEL FOR AIR



FOR AN INFANT, GIVE ONE GENTLE PUFF EVERY 3 SECONDS.



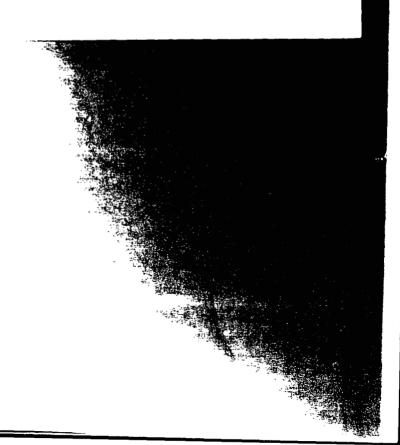
ues, contect your Red Cross chapter for training



RESUSCITATOR: There are various models of oxygen resuscitators available for giving artificial respiration. To operate the oxygen resuscitator on your location, the general procedures are as follows:

- 1. Place a blanket or similar article under the victim's shoulders to facilitate opening the airway. If mouth-tomouth is being administered, the rescuer can continue the head tilt for an open airway rather than using a blanket, etc.
- 2. Oxygen should not be applied to a greasy face due to the danger of spontaneous combustion occurring.
- 3. Open the oxygen cylinder by turning it counterclockwise and check the pressure gauge.
- 4. Make certain the facepiece cushion is properly inflated.
- 5. On the facepiece press the green button to make certain air flow occurs. (through this step another rescuer should have been continuously administering mouth-tomouth to the victim.)
- 6. Place the facepiece firmly over the victim's mouth and nose immediately after an inflation.
- 7. Press the green button to supply a flow of oxygen into the victim's lungs and when his lungs have expanded, release the button keeping the facepiece in place to allow the victim to exhale through the exhalation ports.
- 8. Repeat the lung inflations at the rate of 1 every 5 seconds.
- 9. After the victim begins breathing on his own, keep him in a lying down position and cover only enough to prevent the loss of any body heat.
- 10. Call for medical help/doctor as soon as possible.
- 11. Do Not leave unattended until medical help arrives.

REMEMBER: For the successful execution of an emergency rescue and follow-up first aid treatment, cool headed action is critical. Emergency rescues will not be effective unless YOU are prepared.



Comprehensive monitoring controls hydrogen sulfide in gas-transmission system

E. Tiemstra Nova, An Alberta Corp. Edmonton

Monitoring and controlling hydrogen sulfide (H₂S) in a natural-gas transmission environment requires a comprehensive program. Here are the components for such a program along with a discussion of elements of Nova's gas-transmission unit's control efforts.

Nova's Alberta gas-transmission division (AGTD) is responsible for the gathering, measuring, quality control, and transmission of Alberta natural gas exported from the province.

The AGTD pipeline system consists of 8,745 miles of pipeline, ranging in size from 2 to 42 in., and 38 compressor stations with 544,677 installed hp (Fig. 1). There are 681 receipt points and 93 major delivery points on the system.

More than 75% of marketed Canadian natural-gas production is transported through Nova's facilities.

Specifications for limiting and control of hydrogen sulfide (H₂S) concentrations exist for virtually every company in the business of producing, transporting, or distributing natural gas. These specifications are driven by a number of factors, each of which influences the degree of monitoring and control required.

Safety, corrosion. Effects of H₂S depend upon the concentration and length, of exposure:¹

- 1 ppm—Sulfurous smell clearly detected.
- •40 ppm—Threshold limit value. This is the maximum concentration at which an individual can be exposed for an 8-hr period without adverse effects. Above this limit protective

equipment such as breathing apparatus must be worn.

- 100 ppm—At this concentration, sense of smell is lost in 3-5 min and eves and throat may burn.
- 500 ppm—At this concentration, the effects on the nervous system result in loss of reasoning and balance and will lead to stoppage of breathing within 15 min.
- 1,000 ppm—Exposure at this level results in immediate unconsciousness and leads quickly to death.

A strongly corrosive nature is one of the major reasons for limiting H₂S to very low levels for transmission and distribution. H₂S in the presence of small amounts of oxygen and water forms sulfuric acid which promotes aggressive corrosion of iron-based materials.

A typical requirement to prevent significant H_2S -related corrosion is to reduce H_2S to below the 1.0 grain/ 100 scf level.

Industrial users of natural-gas feedstocks and fuels can be very sensitive to H₂S and total sulfur levels.

Industries requiring low H₂S or sulfur contents include metallurgical furnaces producing low-sulfur alloys or steel, products containing copper or brass, and the making of special glass wares. Fertilizer plants have catalyst beds that can be poisoned by very low levels of sulfur (less than 0.5 ppm), and replacement of the catalyst is expensive.

Similar requirements exist in other petrochemical industries using natural-gas feedstocks.

Contractual requirements. These factors are reflected in contracts addressing the sales and purchase of gas, transportation tariffs, or other transporting agreements. The contracts usually define gas-quality requirements and place tight control on the permissible level of H₂S and total

sulfur in the gas stream.

Typical contractual levels for sales gas in a transmission environment range from 0.25 to 1.0 grains H₂S/100 scf, while specifications for total sulfur are in the 5 to 25 grains/100 scf range.

Total sulfur compounds such as mercaptans do not exhibit the degree of toxicity associated with H₂S and therefore as a group are permitted a higher concentration. From a transmission perspective, there is generally little difficulty in meeting the total sulfur requirements.

Actual concentrations of H₂S and total sulfur in transmission-quality gas are normally well below any contractual specifications. This is particularly true for systems with large numbers of meter stations feeding the system.

Because not all primary production is sour, the mixing of production from sweet wells with sour production at specification levels results in a commingled concentration well below the required concentration.

A final contractual factor that results in a requirement to maintain a high level of monitoring and control is the meeting of differences in the specification of contractual levels of H₂S from the production side right through to the downstream pipeline or end user.

Transporting of natural gas typically involves a number of related contracts including producer/broker contracts, transporter/broker contracts, and dównstream pipeline or end user/broker contracts. All these independent requirements must be consistent or have enough flexibility built into the transmission system facilities to ensure all requirements are met.

Detection equipment

To ensure the H₂S monitoring is met with the resolution, periodicity, and accuracy required, a number of monitoring devices has been developed and are in common use.

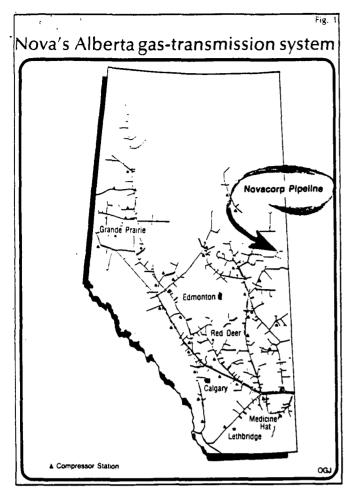
On-line monitors are used in situations requiring continuous, routine review of H₂S concentrations in the gas stream.

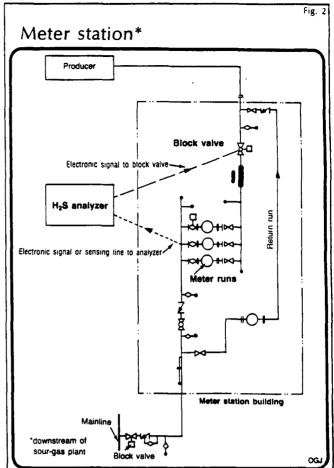
These analyzers find application in monitoring individual receipt stations to enforce gas-quality specifications at the production site, analyzing mainline concentrations to detect off-spec gas not identified at the source, and ensuring merchantable gas is delivered at sales stations.

Lead acetate tape. The principle of the linear change in saids of lead acetate to a brown sulfide in the presence of H₂S is one of the more commonly used approaches to wantify the level of H₂S in gas streams

The sensing element in these types of analyzers is a tape impregnated

Based on a presentation to the 22nd Gulf Coast Measurement Short Course, Houston, Sept. 14-17.





with lead acetate, which is exposed to sample gas under controlled flow rates and conditions.

The H₂S in the gas stream reacts with the lead acetate to produce a stain, and the density (light reflectivity) of the stain is monitored by a photocell. The level of light reflected to the photocell is related to the amount of H₂S in the gas stream.

Operation of this type of analyzer requires filtering of the gas from a sample line and regulation to a fixed flow rate. Excess sample rates are normally used to reduce the time lag while the gas travels from the sample probe to the analyzer.

The gas is then saturated with acetic acid solution at a constant temperature to ensure enough moisture is present to generate a reaction between lead acetate and H₂S and to dissolve any lead carbonates that may have formed on the tape.

The saturated sample gas then proceeds to the measuring cell and sensitized tape. Gas entering the measuring cell passes through or over the tape, reacts with the lead acetate, and

is vented.

The measuring section of the analyzer consists of reference and measuring lamps and photocell detectors. The difference in light levels determined by the photocell observing the

stained tape and that of the reference photocell is proportional to the concentration of H₂S in the gas stream.

To increase the response time of the analyzer, some instruments additionally observe the rate of staining to detect rapid changes in H₂S concentration.

Depending on the application of the analyzer, the output may be directed to a chart recorder for permanent record. The strip chart may serve as a legal document in cases of disputed levels of H_2S concentration or system contamination.

This detection principle is widely used in the gas industry and is a proven, reliable method of determining H₂S levels. The approach is not susceptible to interference effects, and response times are generally in the 3-5 min range.

Light absorption. Absorptive photometric analysis uses the principle of the unique spectrum of light absorbed by sulfur to quantify the concentration in the gas stream. Light or radiation from a source lamp is filtered to remove all wavelengths except the H₂S (sulfur) absorbing frequency, and is directed through a gas sample towards a receiver.

The amount of radiation detected at the receiver depends on the concentration of the H₂S: The higher the H₂S level, the more radiation is absorbed.

This type of analyzer also requires careful control of the sample gas entering the analyzer. Sampling systems include filtering, pressure regulation, and conditioning columns containing packing materials to inhibit other sulfur compounds.

Sample gas enters a cell of known volume, through which a radiation beam is passed. Filters are used to permit only the wavelength absorbed by H₂S to pass through to a photodetector:

The photodetector tube generates a dc-output signal proportional to the radiation intensity which is transmitted to a control module.

The control module compares the photodetector output signal to a reference; the H₂S concentration is proportional to the difference between these signals.

As this system uses packed columns to isolate the H₂S component of the gas stream, the analyzer operates on a sample-and-purge basis of the sampling column. Additionally, the analyzer uses helium to provide a zero check on a periodic basis.

Key features of this detection system include fast response times (typically in the order of 30 sec to 1 min), and the elimination of maintenance problems associated with mechanical sys-

tems and disposable tape.

Interference effects of gas-procssing agents have been observed and as the approach is technically advanced, operation and maintenance of the analyzer require a higher level of expertise.

Electrolytic cell. Titration is another method utilized to determine levels of H₂S and total sulfur in an on-line environment.

This technique utilizes an electrolytic cell with an acid solution (hydrobromic) through which sample gas is bubbled. Platinum electrodes are inserted into the cell and a controlled current is passed through the solution.

At one electrode, hydrogen is generated and escapes with the same gas leaving the cell. Bromine is generated at the other cell, is dissoled in the solution, and reacts with H_2S (and other sulfur compounds) in the sample gas.

A sensing electrode is also included in the cell and is connected across the bromine-generating electrode. When excess bromine is generated, the current in this sensing loop is measured and flows through a switching transistor to turn the generating current off.

The generating current is controlled in this fashion to maintain a specific concentration of bromine in the cell.

Actual concentration of H₂S is determined by a measure of the generating current and a comparison of the average current required when no H₂S exists in the sample. The amount of additional current in excess of the background current is proportional to the concentration of H₂S.

Some factors to consider when this type of analyzer is used include a longer response time and the consumption of the hydrobromic acid solution. The approach is well proven and the analyzer is generally easy to maintain

In addition to the commonly used methods of on-line detection of H₂S, several other approaches are available and serve specific applications. These techniques include gas chromatography, ultraviolet detection chemical sensors (normally used as personal indicators), and electronic sensors. These types of approaches may become more common as the techniques are refined and the applicability to on-ine, remote instrumentation needs is enhanced.

Spot sampling. Gas detector sniffer tubes are used to monitor H₂S levels on a spot-sample basis. These detector tubes contain a specific amount of reagent in a glass tube sealed at both ends.

The tubes are used by breaking off tips at both ends of the tube, installing the tube in a sampling pump, and

drawing in a specific volume of the sample gas.

The chemical reagent in the tube reacts with the sample gas and a color stain develops in the reagent.

Concentration of the gas tested for is determined by the interface of stained/unstained reagent and is read from a calibrated scale on the side of the tube.

Typical accuracies of the tubes are in the order of ±25%. Interference effects can degrade the utility of the tubes, but these effects are usually clearly identified by the manufacturer.

In one specific case of H₂S tubes, interferences can occur from sulfur dioxide, nitrogen dioxide, and mercaptans but only when these compounds are a significant ratio of the H₂S concentration.

There is a wide variety of tubes available for many types of gases and for detection at different concentration ranges. For H₂S, tubes are available for measuring in ranges from as high as 220%, to as low as 5-60 ppm level, with the latter more applicable to transmission-quality gas.

The reaction used for the low level tube is the H₂S-lead acetate reaction to form lead sulfide, which is indicated by a brown stain in the tube.

The reaction is as follows:

H₂S+Pb(CH₃COO)2→PbS + CH₃COOH

Control program

A comprehensive program is required to maintain an effective system of controlling and monitoring production into a transmission system. This program normally encompasses several approaches to ensure all monitoring and control aspects are covered, and the degree to which any particular approach is utilized depends largely on the nature of the transmission system.

A pipeline that has a single receipt and delivery can maintain effective control by analyzing and monitoring at that single point. Pipeline systems with a multitude of receipt points, a mixture of sweet and sour stations, and a large number of delivery stations require a more comprehensive program which would normally include a system supervisory role.

The following section outlines some of the components utilized by Nova to develop an overall H₂S-monitoring program.

Station design and operation. From a transmission viewpoint, the key factor in controlling and limiting H₂S in the system is to control it at the source. For transporters with primary production immediately upstream of the meter station, this requires monitoring the sales-gas stream from the

processing plant.

Effective control requires an appropriate meter-station design which allows for the monitoring of the production, curtailment of the off-spec gas, and the appropriate communication to the system control and production personnel.

Fig. 2 shows a typical layout of a meter station designed for gas coming from a sour-processing plant. Although the gas passing through this facility almost always meets specification, these facilities are intended to prevent an upset at the plant resulting in sour gas being delivered into the transmission system.

A principle incorporated into Nova's facility design philosophy is to make the producer responsible for ensuring that gas-quality specifications are maintained.

If off-spec production is received at our station, production is immediately curtailed, and the producer is responsible for handling of the off-spec gas.

This philosophy of requiring the producer to maintain responsibility and ownership of off-spec (sour) gas translates into specific design features to enforce that requirement.

On-line analyzer

As illustrated in Fig. 2, production from a sour plant is continuously monitored by an on-line analyzer. If H₂S concentrations exceed contract by a small margin (10%), the analyzer sends a signal to the automated block valve, drops the solenoid, and the block valve is closed. This immediately stops the flow into the meter station, and the gas plant is forced to flare or take other appropriate plant operational measures to resolve the problem.

For multiple producers upstream of the station, an approach of an individual analyzer per production stream may be employed. We have adopted a philosophy of dealing with a "commonstream producer" responsible for ensuring gas quality for all production upstream of the meter-station valve.

Once the plant is shut-in, the producer is required to take back all sour gas which has entered the transmission system for retreatment.

This gas is measured through a return run which is sized to meet the plant's capacity to draw gas back, with typical sizes ranging from one-quarter to one-half of the receipt run sizing.

To facilitate the return of sour gas, some station designs have check valves installed so the producer can immediately start the cleanup operation while our called-out operator is enroute. Stations without the check valve must wait until field personnel

are on site to open the appropriate valves and monitor the operation.

Nova's guideline is to require the plant to return about twice the volume of sour gas that entered the system. This guideline is used to ensure adequate cleanup has occurred and is confirmed by field personnel taking sniffer checks of the return gas.

Analyzer response time. Another consideration is to ensure no sour gas escapes into a mainline or is washed downstream by other production in the area. Meeting this requirement depends on the response time of the H₂S analyzer.

"Bottle-piping" ensures that while the analyzer is processing a shut-in sequence, sour gas at the station does not escape into the mainline. Because typical response times for H₂S analyzers range from 30 sec to several minutes, a considerable volume of sour gas can escape into the system if this effect is not addressed.

The amount of downstream piping required before connection to another lateral or mainline or to any other critical location (sales tap) can be easily calculated given maximum production rates, analyzer response times, and worst-case operating pressures and temperatures.

Essentially, the volume of downstream piping must exceed the actual volume of sour gas that can enter the station while the analyzer is processing a shut-in sequence.

This calculation can be expressed as pipe volume = production rate at line conditions × analyzer response time.

A worst-case calculation assumes production is at the maximum rate, line conditions are at the lowest expected pressure and highest expected temperature, and the response time is the total time for the analyzing system to enact a shut-in sequence.

In order to reduce the amount of downstream piping, efforts to improve the response time of the analyzing system are required.

These include selection of equipment with fast response times, reducing the length of sampling lines, locating the analyzer as far upstream of the meter station as possible, and ensuring any sales taps are not installed within a critical distance of the meter station.

In some cases, even the optimization of the analyzer response time is insufficient to protect the facility. These cases typically occur in retrofit or conversion situations and may require a considerable volume of pipe to be installed.

This bottle-piping may consist of several loops of pipeline to meet the response-time objective. Installation of bottle-piping is generally a last-resort measure due to the high cost.

A final design consideration is analyzer reliability. All instrumentation is subject to failure which may allow sour gas to enter the pipeline undetected and lead to significant disruption to processing plants.

In the case of failure to detect sour production, the effects may include H_2S exposure to consumers or the contamination of volumes delivered at major sales stations.

False shut-in of the processing plant causes a number of operational difficulties for the plant personnel and may result in large volumes being flared.

Overcoming these concerns requires a program of sound maintenance as a first measure and in special cases may require redundant instrumentation.

Depending on how the shut-in logic is sequenced (parallel vs. series operation), the effect can be to reduce the false shut-in rate to the plant at the expense of increased risk of system-contamination, or vice-versa. Fault-tree analytical techniques can be used to quantify these effects.

Field monitoring. Meter stations added to the transmission system are screened at the design stage for the handling of production from a sour field. However, the drilling of new wells, the addition of new production, or the decline of existing production can result in a so-called "sweet facility" turning "sour."

To ensure sour production is not added to the system without adequate protection equipment installed at the meter station (H₂S analyzers, etc.), Nova conducts spot checks of all sweet meter stations on a periodic basis.

For new meter stations being brought on-line, spot samples with sniffer tubes are taken once a week. Once this initial sampling has occurred and the station is well below specifications, sniffer checks are reduced to once a month as a routine operation.

In the event a spot sample indicates the presence of H_2S in excess of 75% of the contract specification, Nova installs a portable on-line analyzer at the station to provide continuous monitoring. The analyzer remains at the station for a specified period to obtain a representative indication of the H_2S levels in the sales-gas stream.

If the portable analyzer or subsequent sniffer checks identify concentrations of H₂S violating the contractual specification, the plant is warned to ensure measures are in place to meet gas-quality requirements.

A second violation of the specifica-

tion results in a plant shut-in until facilities are in place to ensure no sour gas escapes into the transmission system.

The meter station is then converted to a sour facility and equipped with a permanent H_2S on-line analyzer, a return run (for returning sour production to the plant), an automated block valve, and sufficient bottle piping to meet the response-time requirements of the analyzer.

Laboratory monitoring. Another method of monitoring utilized by Nova is laboratory sampling.

Routine gas samples are obtained at all meter stations to determine heating value and gas composition, and this affords the ability to provide additional monitoring for total sulfur.

Although the degradation of sulfur compounds in steel and stainless-steel sample cylinders is recognized, the use of titration techniques and cylinder sample gas provides a practical method of checking total sulfur levels.

Degradation of the sulfur in the cylinders has been determined to be in the order of 50% in a 2-4 week period. Rather than check for total sulfur at all field facilities (extensive travel time), only facilities exceeding 50% of the contract specification as tested by the laboratory are field tested.

In Nova's experience, little difficulty is seen in meeting total sulfur requirements. Sour production in our areas has a very high H₂S constituent in the sulfur compounds and, combined with relatively high contractual limits (5-20 grains/100 scf total sulfur), has resulted in no requirement for online monitoring of total sulfur at the source.

System-wide monitoring. In a transmission system remotely operated via a supervisory control and data acquisition (scada) system, H₂S monitoring can be maintained. This monitoring provides a system-wide review of the real time levels of H₂S in the system and allows for effective operational control to ensure system deliveries are within gas-quality requirements.

Nova employs monitoring at this level to perform two functions.

The first function is to identify specific receipt stations that have exceeded contractual levels and have been shut in by on-site instrumentation. The second allows for a system-wide review of mainline H₂S concentrations and ensures deliveries meet gasquality requirements.

Station monitoring is primarily one of identification and communication on an individual station basis. Stations that are telemetered and equipped to handle production from sour plants have the ability to generate alarms in

The author. .



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the gas-control (remote operations) center.

Alarming can take several forms from the generation of software-driven alarms based on an analog value at the gas-control site, to the transmitting of alarm indications from the analyzer itself.

Analog information usually provides greater detail and direct access to operating history, but binary alarms suffice on an individual station basis. Additionally, the producer is often provided with signals from the station analyzer as a check on plant instrumentation.

Alarms typically include three separate indications:

 H₂S failure. This alarm is driven by self-diagnostics incorporated into the analyzer and includes indication of low photodetector voltages, failure to auto-zero or power-supply interruptions.

While the analyzer is in a known failed state, the station is unprotected and the response from gas control is to dispatch field personnel immediately to restore the analyzer to service.

• H₂S warning. This indication alerts Nova's gas control to a potential plant upset and is initiated by the analyzer when the H₂S level has reached 80% of the contract limit.

The action taken by gas control is to notify the plant personnel of the warning indication and allows the plant to take corrective action to prevent total shut-in.

• H₂S emergency. This alarm identifies a situation where the plant has produced off-spec gas and is now shut-in. Operations personnel are immediately sent to the station in question to ensure sour gas has not escaped into the system (in the event the block valve failed to close) and to initiate operations to return sour production to the plant.

Supervisory monitoring. The second function is one of system-wide supervisory monitoring.

System-wide levels of H₂S are monitored by telemetering analog values of analyzers distributed throughout the system. Typical locations for monitoring mainline H₂S levels include major receipt stations, major delivery stations, compressor stations, or border stations.

Analyzers at these sites provide continuous reporting of H₂S levels flowing past the point. Review of system trends and abnormal increases in mainline levels alerts gas-control personnel of potential system contamination.

The development of a system-wide monitoring program requires adequate instrumentation to identify the approximate location of the source of the problem and to allow enough time for effective management of the problem.

Contamination. In the event the plant has a sour upset and the automatic shut-in equipment at a meter station fails to function properly, there is the potential to receive off-spec production into the transmission system.

Although this situation is rare, the problem can be severe as the upset may result in sour wellhead gas (in the order of % H₂S rather than ppm) being delivered into the system.

This problem is compounded when there are sales taps or delivery stations immediately downstream of the sour plant, and the potential exists to expose the consumer to high-concentration H₂S. Clearly, methods to mitigate or eliminate this exposure are required.

If sour gas has entered the system, action must be taken immediately to reduce any potential risks associated with the sour gas.

This action includes ensuring the gas is not delivered to downstream meter stations or sales taps and ensuring appropriate protection is used by field personnel. Deliveries may be interrupted and the system operating configuration changed immediately.

Process steps. A major objective in addressing the situation is to capture the sour gas and dilute the concentration to acceptable limits.

The activities associated with the capture-and-blend process include:

• Identification of the problem. Precise identification of both the concentration and source of the contaminant depends upon sufficient numbers of analyzers to monitor mainline-gas quality.

Even with a reasonable level of instrumentation, the problem may only be detected by system-control personnel when the level has exceeded alarm limits on a mainline analyzer.

• Location of the sour gas. The next step is to determine the location of the sour gas. Although there is some blending and dilution of the sour gas as it travels down the pipeline, it normally remains in a continuous section.

Measures that can be used to determine the location between mainline analyzers include hydraulic modeling of the system and sniffer checks taken at mainline block valves by field operations personnel.

Hydraulic modeling can provide a good estimate of the location of the sour gas, if information on flow rates and the time the upset occurred is available.

Capture of the sour gas. The ability to capture the sour gas and prevent it from being delivered to downstream pipelines or sales stations depends largely on the facilities and the amount of time available.

For looped pipeline systems (i.e., parallel lines with regular block valve and crossover connections), the normal approach is to identify a section of looped line into which the sour gas can be routed and captured.

Actual capture procedures depend on the specific facilities in place, but in general field personnel would be dispatched to the location chosen to isolate the sour gas and valve off one of the loops to force the gas through one line. Field personnel would then monitor for the approach of the sour gas by taking periodic sniffer checks.

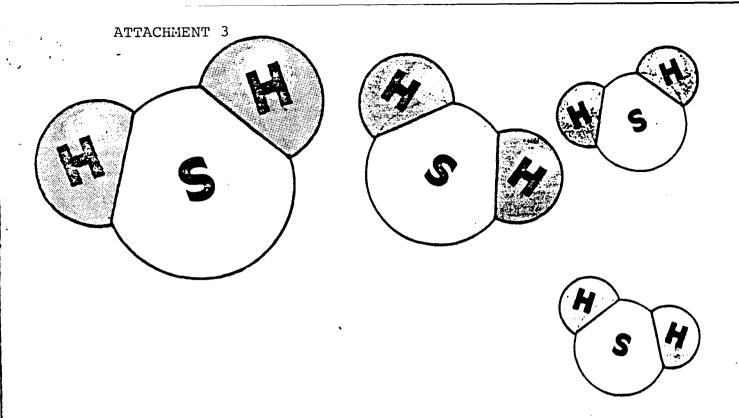
Once the section of sour gas has been detected, the appropriate crossover or mainline block valve would be operated to capture the sour gas and to allow sweet mainline flows to resume flow in the other loop.

• Blending to acceptable levels. Once isolated in a section of loop, the H₂S can be diluted to acceptable levels by blending the sour gas into the main sweet stream. This blending is normally accomplished by partly opening a downstream crossover valve and controlling the flow rate so that the downstream concentration of H₂S is within contract.

Monitoring is accomplished by taking sniffer checks periodically and any time after the blending valve is adjusted. It is critical to ensure the H₂S is diluted to within spec on a continuous basis, or the problem has not been resolved and may require a further capture-and-dilution attempt downstream. Once the sour gas has been fully diluted and sweet mainline gas is observed in the containment loop, the system can be returned to normal.

Reference

Canadian Association of Oilwell Drilling Contractors, "Hydrogen Sulphide Training," April 1979



Part 1 — Introduction

Overcoming the complexities of safely working with H₂S is a monumental technological task. Economically speaking, the problem is a staggering one. Educating personnel requires specialists with a practical understanding of industry operation and a detailed knowledge of sour gas effects under different circumstances.

Engineering and design characteristics required for energy development in H_zS areas necessitate use of the most skilled technicians for laboratory analysis and field testing. Tools and tubulars must be specially trimmed. Normal operating procedures must often be altered and additional time taken to accomplish otherwise routine tasks. These procedures and the special metallurgical requirements are costly.

This series of articles will deal with specific industry considerations ranging from safety and training to metallurgical and design criteria. It will demonstrate the magnitude of H₂S problems and the extent to which the petroleum industry is pioneering engineering concepts and operational procedures.

New and deeper producing zones containing hydrogen sulfide (H₂S) up to lethal levels, demand rigorously safe operating practices in both drilling and production. And older reservoirs, now under secondary or tertiary recovery, are generating or releasing this dangerous gas where its presence was not previously recorded.

Hydrogen sulfide is toxic and corrosive. It occurs naturally in many geologic formations and is formed primarily by decomposition of organic matter containing sulfur. Its characteristics are given in Table 1.

Often termed sour gas, H₂S is found in many areas throughout the U.S. Examples are:

- Smackover formation along the Gulf of Mexico coastline.
- Tuscaloosa formations along the Louisiana-Mississippi coast.
- Overthrust Belt in the Rocky Mountain area.
- West Texas areas involved in secondary recovery operations.

Rules and regulations are now strict with respect to drilling and production. Government agencies responsible for these rules not only include OSHA but other federal and state agencies such as the USGS and the Texas Railroad Commission. Strict regulations involving both operations and training were promulgated as an aftermath of several tragic fatal incidences of accidental population exposure to the gas, as well as the need for safe practices with respect to oil field personnel.

TABLE 1. Characteristics of hydrogen sulfide gas

- 1. H₂S gas is colorless.
- 2. The characteristic odor is that of rotten eggs. However, it is imperative to understand that relatively low concentrations of hydrogen sulfide gas deaden the olfactory nerves which regulate the sense of smell as a detection tool. These concentrations are approximately 50 ppm.
- Specific gravity of the gas is 1.192 which is greater than air (1.000). Therefore, the gas will tend to settle in low areas such as the substructure cellar and near mud pits.
- 4. The gas forms an explosive mixture with air in the ranges of 4.3% to 45%concentrations. This is particularly dangerous when compared to methane which is combustible in the 5% to 15% range.
- Hydrogen sulfide has an ignition temperature of 500 F as compared to 1,000 F for methane.
- The gas burns with a blue flame but produces sulfur dioxide, another toxic gas.
- 7. H₂S is soluble in water, producing a weak acid.

TABLE 2. Effects of hydrogen sulfide on personnel		
Concentration, %	ppm	Effects
0.001	10 .	Can smell; safe for 8 hours.
0.01	100	Kills smell in 3 to 15 min; may burn eyes and throat.
0.02	200	Kills smell quickly; stings eyes and throat.
U. 05	500	Loss of balance; respiratory difficulties in 30 to 45 min.
0.07	700	Unconscious in less than 15 min; death will occur if not rescued promptly; immediate artificial resuscitation required.
0.1	1,000	Permanent brain damage if not rescued immediately.

Physical Effects

The effect of exposure to H₂S depends on:

- Concentration level of the gas.
- Length of exposure.
- Previous health condition of the individual.

Since H₂S attacks the respiratory and nervous systems, individuals with previous physical disorders are more likely to have a lower resistance to H₂S poisoning than those without respiratory or nervous ailments.

Effects of H₂S exposure are listed in Table 2. Note that an exposure of very small concentrations in the range of 500 to 600 ppm can be fatal in a short time.

Brief exposure to H₂S at low concentrations has caused conjunctivitis and kevatitis while exposure at high concentrations has caused unconsciousness, respiratory paralysis, and death. Conclusive evidence of adverse health effects from repeated, long-term exposure to H₂S at low concentrations has not been found. However, there is some evidence that exposure at low concentrations or in combination with other chemical substances such as hydrocarbons may cause nervoussystem, cardiovascular, and gastrointestinal disorders.

There are no pharmaceutical antidotes to H_2S poisoning. If a person is overcome by H_2S , rescuers using proper respiratory equipment should remove the victim to a safe upwind area from the contamination. Since

H₂S deprives the victim of oxygen, it becomes necessary to supply fresh, uncontaminated air to the gassed victim. If the victim's breathing has ceased, prompt artificial respiration must be administered. When the victim recovers, he should continue to be observed and transferred to a medical facility for professional medical attention.

Effects Of H₂S On Metal

The basic reaction that takes place when iron is exposed to moist H₂S can best be seen by the formula presented below.

Fe +
$$H_2S$$
 Fe S_3 + 2H

This basic reaction will create atomic hydrogen in the system and can cause many corrosion problems depending on the circumstances.

The three predominant types of corrosion of concern are hydrogen blistering, hydrogen embrittlement, and sulfide stress corrosion. Each of these will be considered in detail in a future article. Blistering in its simplest form is actually the formation of blister on the iron surface due to continued exposure to excessive hydrogen ions in a corrosive environment. This usually occurs on metals with low yield strengths.

Hydrogen embrittlement is of greater concern because it occurs within the microstructure of the iron and cannot be readily seen. Embrittlement occurs when atomic hydrogen accumulates in the voids of crystal defects or stress-induced microfractures of nonductile steel of high strength or hardness and increases internal pressure until the yield strength is exceeded. Hydrogen embrittlement is similar and, in the drilling industry, is often considered synonymous with sulfide stress cracking.

The type of H₂S corrosion encountered will depend on many factors:

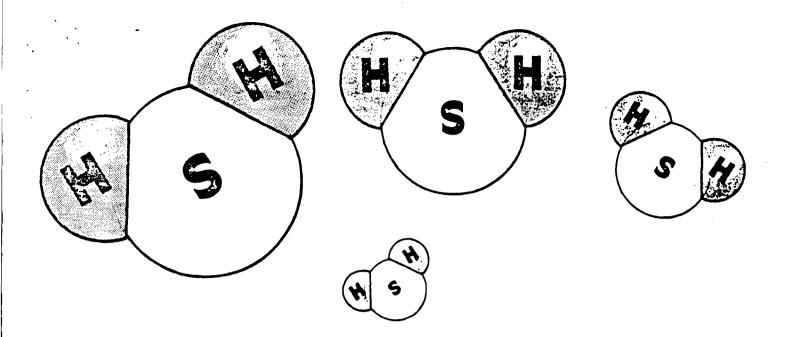
- Yield strength of the metal.
- Type of metal.
- Rockwell hardness.
- Stress level encountered.
- H.S concentration.
- Temperature at which the metal is exposed to H₂S.
- Actual environment in which the iron is placed.

About the Authors

Neal Adams, who has instructed a number of schools in the fields of well control and hydrogen sulfide safety, has written numerous articles relating to drilling problems as well as the soon-to-be-released book "Well Control Problems and Solutions."

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Part 2—Rules And Regulations

The petroleum industry is faced with many state and federal regulations concerning drilling and production in known or suspected sour gas areas. Most state regulations are designed to protect the public while federal regulations basically are designed to protect the employee and deal primarily with the selection and use of respiratory equipment.

OSHA

The Occupational Safety and Health Administration (OSHA) states, "Respirators shall be provided by the employer when such equipment is necessary to protect the health of the employees. The employer shall provide the respirators which are applicable and suitable for the purpose intended. The employer shall be responsible for the establishment and maintenance of a respiratory protective program which shall include the requirements as set forth in 29 CFR 1910.134." ¹

These requirements call for an 11-point program that an employer must follow in order to meet the regulation's minimum requirements. Some of these cover categories such as selection of respirators, maintenance and training requirements, assignment and storage of respirators. Others cover surveillance of the work area and the capability of an employee to work in respiratory equipment.

In the selection of respiratory equipment, the regulation states that proper selection shall be made according to the guidance of American National Standard Practices for Respiratory Protection Z88.2-1969. Today, respirators authorized for use in an H₂S environ-

	TABLE 1. Tolerance limit value
-	Material Acceptable colling
	average concentration
	H _s S 20 ppm
1.14	Acceptable maximum peak above acceptable
	concentration for 8-hr shift
72.	Concentration Maximum duration
	50 ppm 10 min once and only if no other
	measurable exposure occurs
•	and green file to the file and supplied the control of the control

ment must be certified according to requirements set forth by the National Institute of Occupational Safety and Health (NIOSH) and Mine Enforcement Safety Administration (MESA). If a unit does not bear a NIOSH/MESA certification number, it is not authorized for use in an H₂S environment. This authority was given NIOSH by 30 CFR 11.

The training requirements simply state, "The user shall be instructed and trained in the proper use of respirators and their limitations." Possible future requirements are discussed in the following section.

NIOSH

The question of when an employer must provide the employee with respirators is mandated by NIOSH. NIOSH has stated that no employee shall be exposed to H.S above the tolerance limit value (TLV) — 29 CFR 1910, Tables x, y, and z. The TLV for H.S is 10 ppm or 1/1000 of 100%. When the possibility exists that H.S may be encountered above this concentration,

proper respiratory equipment must be readily available (Table 1)

Currently in committee is a NIOSH publication that may soon become a hydrogen sulfide standard and as such will affect the drilling industry. The Department of Health, Education and Welfare document is entitled, Criteria for a Recommended Standard for Occupational Exposure to Hydrogen Sulfide.² The following are some of its recommendations.

Workplace — Exposure to hydrogen sulfide shall be controlled so that no employee is exposed to hydrogen sulfide at a ceiling concentration greater than 15 mg of H₂S/cu meter of air (10 ppm) as determined with a sampling period of 10 min for up to a 10-hr work shift in a 40-hr week. Evacuation of the area shall be required if the concentration of H₂S equals or exceeds 70 mg/cu meter (50 ppm).

Medical — Medical surveillance shall be made available to all workers subject to occupational exposure to H.S. Pertinent medical records shall be maintained for all employees who are involved in the manufacturing, processing, or handling of H.S or are in any other way exposed to it in the workplace. Such records shall be kept for at least 30 years after termination of employment.

Personal protective equipment — When use of a respirator is permitted or required under emergency conditions, it shall be selected in accordance with the specifications in Table 2³ and shall comply with the standards jointly approved by NIOSH and MESA. The respiratory program must meet the requirements as set forth in 29 CFR 1910.134.

Training — Training in respiratory protection shall include actually wearing and using the equipment. Training in respiratory equipment shall be started before a worker goes on the job and shall be repeated at least quarterly and each time a new crew is formed. All members of a crew should receive the same training even if some have had a previous training session in the same quarter.

Monitoring — Provisions must be made to institute a program of personal monitoring to determine the ceiling exposures of each employee occupationally exposed to H₂S. Source and area monitoring may be used to supplement personal monitoring.

Alarm and evacuation — Monitors must be set up that will give an alarm signal when 70 mg/cu meter (50 ppm) is detected.

Fixed monitors shall also have a different alarm to signal the presence of H₂S at concentrations of 15 to 70 mg/cu meter (10 to 50 ppm).

ANSI

Many of the federal regulations are based on the standards set forth by the American National Standards Institute (ANSI). Before development of the NIOSH and OSHA Decision Logic, the ANSI Z88.2-1969 Standards were the main source of information on respirator selection. Today, selection of respirators is based on those which have been found to meet established performance criteria and listed as approved by an authority such as MESA or NIOSH.

The U.S. Bureau of Mines (USBM) no longer tests and approves respirators. That responsibility is now

for hydrogen sulfide*		
Concentration	Respirator type approved under provisions of 30 CFR 11	
Less than or equal to 70 mg/cu meter (50 ppm)	Any supplied-air respirator with full facepiece. Any self-contained breathing apparatus with full facepiece.	
Greater than 70 mg/cu meter (50 ppm)	1. Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive-pressure mode. 2. Combination Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive-pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.	
Emergency (entry into area of unknown concentration for emergency purposes, e.g., firefighting)	1. Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive-pressure mode. 2. Combination Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive-pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.	
Escape (from an area of unknown concentration)	 Any self-contained breathing apparatus. Any gas mask providing adequate protection against hydrogen sulfide (not to bused in confined spaces). 	

shared by MESA and NIOSH who jointly test and approve respirators under the provisions of a respirator and approval document, 30 CFR Part II.

Both NIOSH and ANSI recognize hydrogen suifide as a gas which is immediately dangerous to life and health at relatively low concentrations. Based on this, the only respirators available for use are self-contained breathing apparatus (SCBA) that operate in the pressure-demand mode or hose line units which create positive pressure inside the facepiece. Table 2 is a guide for the selection and use of respirators in an H₂S atmosphere.

USGS

The U.S. Geological Survey (USGS) has its own regulations concerning the drilling of wells in an H.S environment. In addition to known sour areas, some precautions must be taken on all frontier wells and some wildcat wells. This document, GSS-OCS Order 2, applies to all wells drilled in U.S. waters.

Due to the many confined and enclosed quarters on most offshore vessels and rigs, the possibilities of H.S accumulation build ups above lethal levels are far greater than those on land. Because of this and the fact that there is no place to escape from a sudden release of H₂S. OCS Order 2 is by far the most stringent H₂S regulation confronting most operators.

For example, most of the other state and federal

regulations are rather vague about monitoring equipment. OCS Order 2, on the other hand, states very simply that the monitoring equipment shall be capable of sensing a minimum of 5 ppm H₂S in air with sensing points located at the bellnipple, shale shaker, mud pits, driller's stand, living quarters, and any other areas where H₂S might accumulate in hazardous quantities.

Other areas which receive the same strict requirements are training of employees, metal and sulfide stress corrosion, H₂S serviceable equipment, conditions when employees must wear protective breathing apparatus, emergency conditions and procedures, mud rheology and conditioning, and other requirements pertaining to protection against H₂S. Due to the depth and nature of this article, it is impossible to discuss the entire regulation. It is very easy to comprehend in comparision to many regulations, however, and leaves no doubt about what is expected of the operator. OCS Order 2 should be followed carefully, especially if there is a chance of drilling into H₂S. The USGS has checked frequently and will enforce all aspects of this regulation.

One other federal document that warrants some discussion is a relatively new regulation known as the USGS Notice to Lessee No. 10 (NTL-10). This regulation applies to known or suspected sour fields and all wildcat operations on federal lands. For all practical purposes it is a duplication of Texas Railroad Commission Rule 36, and at the time of this writing it is not enforced.

TRC Rule 36

This document warrants some discussion because it not only applies directly to the state of Texas, but applies indirectly to many other states as well. Some states that do not have formal regulations governing the drilling of known or suspected sour gas wells use this regulation as a guideline for certain compliance procedures. The overriding factor is protection of the general public. The degree to which an operator must comply depends on the radius of exposure based on the calculated concentration of hydrogen sulfide and the rate at which H₂S is expected to flow from the well.

For all operations subject to Rule 36 (except in the case of storage tanks), the radius of exposure is determined by the following Pasquill-Gifford equations

or by other methods that have been approved by the commission.

For determining the location of 100 ppm radius of exposure:

 $X = [(1.589) \text{ (mole fraction of } H_2S) (Q)] 0.6258$

For determining the location of 500 ppm radius of exposure:

 $X = [(0.4546) \text{ (mole fraction of } H_2S) \text{ (Q)}] 0.6258$ where:

X = Radius of exposure, ft

Q = Maximum volume determined to be available for escape, cfd

H₂S = Mole fraction of H₂S in the gaseous mixture available for escape

Once calculated, the radius of exposure will determine to what extent the operator must go to protect the public, his crews and rig equipment. It may be interesting to note that on wildcat operations and areas where insufficient data exist to calculate a radius of exposure, a 100-ppm radius of exposure equal to 3,000 ft will be assumed. With known or suspected H₂S wells, all protective equipment must be rigged up, crews trained, and a contingency plan approved by the Texas Railroad Commission prior to entering a zone 1,000 ft above the formation containing hydrogen sulfide.

At present, Rule 36 is being studied by the Railroad Commission and the industry. Some changes will be made that affect drilling procedures and precautions to be taken on sour gas wells.

Most of the present rules regarding sour gas operations are relatively reasonable. They require precautions that any prudent operator would follow even if the regulations did not exist. And if the rules are adhered to at all times, the chance of accidental and dangerous exposure to H₂S will be greatly diminished.

References

- OSHA: Occupational Safety and Health Standards for General Industry, 29 CFR 1910 (1978) 128.
- DHEW (NIOSH): Criteria for a Recommended Standard for Occupational Exposure to Hydrogen Sulfide, publication No. 77-158.
 OSHA: Table Z-2 (a) (3), 29 CFR 1910, Table 2, p. 1001.
- 4. DHEW: A Guide to Respiratory Protection, 30 CFR, Part II (1976) 52.

APPENDIX B

AN APPENDIX TO AN ORDER OF THE KENTUCKY PUBLIC SERVICE COMMISSION IN CASE NO. 96-087 DATED MARCH 14, 1996

INTRA-AGENCY MEMORANDUM

KENTUCKY PUBLIC SERVICE COMMISSION

TO:

B.T.U. Pipeline, Inc. File

THROUGH:

E. Scott Smith, Manager Cas Pipeline Safety Branch

Larry L. Amburgey, Investigator Supervisor LLA

Gas Pipeline Safety Branch

Ralph E. Dennis, Manager

Gas Branch

FROM:

David B. Kinman, Gas Utility Investigator DC Gas Pipeline Safety Branch

Earl H. Alderman, Jr., Gas Utility Investigator

Gas Pipeline Safety Branch

DATE:

February 8, 1996

SUBJECT: Hydroge

Hydrogen Sulfide (H₂S) in B.T.U. Pipeline, Inc. (B.T.U.)

System

On January 31, 1996, Earl H. Alderman, Jr. and David B. Kinman, Public Service Commission safety investigators, accompanied by Mike Gamble of B.T.U. visited the B.T.U. system in order to test the gas for the presence of $\rm H_2S$.

An inspection on January 25, 1996, had shown a hazardous amount of $\rm H_2S$ of 1,000 parts per million (ppm) in the system. Mr. Richard Williams of B.T.U. subsequently shut off the Stevens' well which was the source of the $\rm H_2S$.

Tests taken on January 31, 1996, found that the level of $\rm H_2S$ had dropped from 1,000 ppm to 200 ppm.

Tests taken by Mr. Alderman on February 8, 1996, indicated on the Draker tubes used to test for H_2S , that the level has continued to fall. The present level on February 8, 1996 is in excess of 60 ppm, but less than 100 ppm. It is not possible for us to determine the exact amount of H_2S present when it falls into these ranges as the upper level of one tube is 60 ppm and the lower level of the next tube is 100 ppm.

It does appear that the level of H2S is falling.

DBK: EHA: dcp

9602100/9602900/96030000/9603100